

Dedicated to Professor Ionel Haiduc
on the occasion of his 80th anniversary

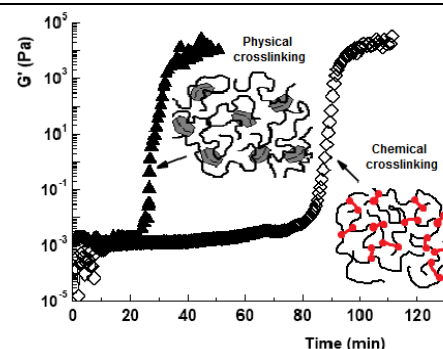
IN-SITU MONITORING OF *N-t*-BUTYLACRYLAMIDE POLYMERIZATION IN PRESENCE/ABSENCE OF CLAY

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Polymerization of *N-t*-butylacrylamide at 20 °C in the presence of Laponite RD (as physical crosslinker) or *N,N'*-methylenebis(acrylamide) (as chemical crosslinker) was investigated by turbidimetry and rheology. Ammonium persulfate and *N,N,N',N'*-tetramethylethylenediamine were used as initiator and catalyst, respectively. Addition of physical or chemical crosslinker determines the increasing of the induction period of polymerization process. A longer time of polymerization induction was observed for clay/monomer ratios between 0.20 and 0.35. Both elastic (G') and viscous (G'') moduli were followed during the redox polymerization and their plateau values were estimated. The loss tangent, $\tan \delta (=G''/G')$, was found to be lower than 1 for all investigated samples suggesting a network structure. For clay/monomer ratio between 0.25 and 0.35, the entangled polymer network strength is higher than that corresponding to the sample obtained in the presence of *N,N'*-methylenebis(acrylamide).



INTRODUCTION

In the last decades, the materials based on *N*-substituted acrylamides have attracted an increasing attention due to their capacity to undergo changes in volume in aqueous medium as response to a thermal stimulus.¹⁻⁶ The thermosensitivity of different hydrogels containing poly(*N*-substituted acrylamide) differs, depending on the chemical structure of polymer components.⁷ For example, poly(*N*-isopropylacrylamide), which is a water soluble polymer, shows a phase transition temperature at 32°C – 34°C while poly(*N-t*-butylacrylamide) is not soluble in water and does not exhibit the thermosensitivity. The combination of the two acrylamide derivatives in different ratios allows the

design of hydrogels with modified transition temperature as compared to components alone. Thereby, poly(acrylamide) hydrogels containing 60% *N-t*-butylacrylamide (*N-t*-BAA) exhibits thermal response in the range 10°C – 28°C although the two homopolymers do not present phase transition temperature.¹

N-t-butylacrylamide (the monomer) is water soluble and its solubility improves as the temperature increases,⁸ but poly(*N-t*-butylacrylamide) is insoluble in water due to the hydrophobic $-\text{C}(\text{CH}_3)_3$ groups from its structure. An increased solubility is obtained in water/ethanol mixtures with high content of ethanol and the pure ethanol behaves as a good solvent for the polymer.¹

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N-*t*-butylacrylamide is often used for obtaining amphiphilic polymers by copolymerization with some hydrophilic polymers.⁹⁻¹¹ The hydrogels based on acrylamide derivatives have a network structure, generally formed by chemical crosslinking by using an organic crosslinker, e.g. *N,N'*-methylenebis(acrylamide) (MBA).¹² The disadvantages deriving from the use of a chemical crosslinker in the hydrogels obtaining (mechanical fragility, low swelling, turbidity, etc.) can be eliminated by replacing it with a clay which acts as a physical crosslinker.¹³⁻¹⁶

Laponite RD (LRD) is a synthetic clay which disperses in water as disk-like particles with the thickness of 1 nm and the diameter of about 30 nm. In water, the LRD disks have a strong negative charge on the faces and a weak positive charge on the rims.¹⁷⁻²⁰ By addition of a polymer into LRD dispersion, the interactions between clay particles are changed due to adsorption of the macromolecular chains on the surface of clay platelets.^{21,22}

The aim of the present paper is to study in-situ redox polymerization of *N*-*t*-BAA in presence/absence of physical/chemical crosslinker by using rheology and turbidimetry. The influence of a chemical (MBA) or physical (LRD) crosslinker on the polymerization induction time and on the entangled polymer network strength (given by the viscoelastic moduli corresponding to the plateau obtained when the polymerization is finished) was followed. Starting from homogeneous mixtures (monomer in water/ethanol mixture in presence/absence of clay or *N,N'*-methylenebis(acrylamide)), precipitation polymerization systems were developed and investigated.

RESULTS AND DISCUSSION

The polymerization of *N*-*t*-BAA initiated with ammonium persulfate (APS) as initiator and *N,N,N',N'*-tetramethylethylenediamine (TEMED) as catalyst was investigated by rheology or turbidimetry. The compositions of all reaction mixtures investigated in the present study are shown in Table 1.

In Fig. 1 is shown the evolution of the rheological parameters (G' and G'') during the radical polymerization of *N*-*t*-BAA in the presence of APS and TEMED and in the absence/presence of physical or chemical crosslinkers.

It can be observed that the induction period of polymerization depends on the reaction conditions, i.e., the presence and the type of crosslinker. Thus, in the presence of APS/TEMED redox initiation system, the polymerization starts after about 10 min and the addition of MBA as chemical crosslinker increases the induction period at about 80 min. In the presence of APS, TEMED and LRD, the induction period for *N*-*t*-BAA polymerization was found as being approximately 25 min. Our data concerning the induction period are in agreement with those obtained by Okay and Oppermann,²³ which have estimated, also by rheological measurements, an induction period between 3 min and 10 min for the polymerization of acrylamide in presence of LRD, APS and TEMED. The induction time for the *N*-*t*-BAA polymerization in presence of LRD (present data), is slightly higher probably due to the steric effect of the *t*-butyl substituent.

Table 1

LRD/*N*-*t*-BAA and MBA/*N*-*t*-BAA ratios used in the polymerization of *N*-*t*-BAA^a and the plateau viscoelastic parameters^b

Sample ^c	LRD/ <i>N</i> - <i>t</i> -BAA (wt/wt)	MBA/ <i>N</i> - <i>t</i> -BAA (mol/mol)	G'_p (Pa)	Std. error (Pa)	R^2	G''_p (Pa)	Std. error (Pa)	R^2	$\tan \delta$ (G''_p / G'_p)
1	0	0	13700	388	0.930	8862	257	0.921	0.65
2	0.20	0	9655	420	0.891	7765	152	0.985	0.80
3	0.25	0	1175	110	0.985	263	25	0.988	0.22
4	0.30	0	3653	159	0.973	764	18	0.969	0.21
5	0.35	0	9150	825	0.972	1353	95	0.917	0.15
6	0	0.1	15996	225	0.983	7028	342	0.931	0.44

^a all reaction solutions contain 0.6 g *N*-*t*-BAA, 0.032 g APS and 0.098 ml TEMED;

^b the plateau rheological parameters (G'_p and G''_p in the final stage of the reaction, but before the polymer separation from the reaction medium) were established by fitting the rheological data with the following logistic sigmoidal equation using an Origin 6.0 software:

$G(t) = ((G_i - G_p) / (1 - (\frac{x}{x_0})^a)) + G_p$, where $G(t)$ represents the rheological parameter at time t , G_i and G_p are the viscoelastic parameters at initial time and plateau, respectively;

^c three samples with LRD/*N*-*t*-BAA = 0.10; 0.28; 0.40 and MBA/*N*-*t*-BAA = 0 were prepared and investigated only by turbidimetry;

they are not included in the table.

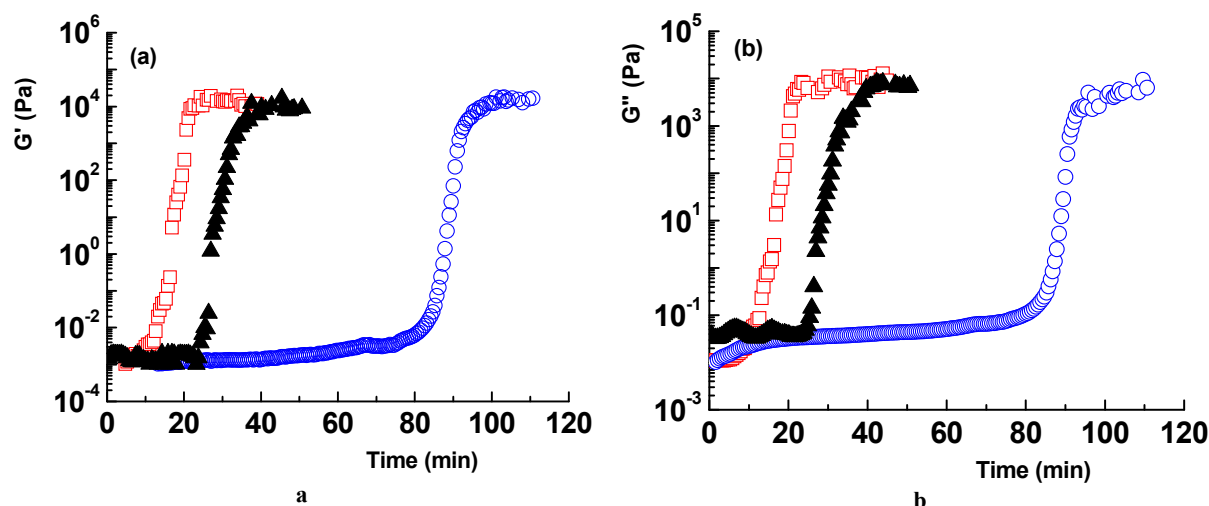


Fig. 1 – Variation of (a) elastic and (b) viscous moduli during the radical polymerization of N-t-BAA in absence of crosslinker (\square), in presence of chemical crosslinker, MBA (MBA/N-t-BAA=0.1 mol/mol) (\circ) and physical crosslinker, LRD (LRD/N-t-BAA=0.20 wt/wt) (\blacktriangle).

The delay of the polymerization reaction in the presence of chemical crosslinker could be explained by slowing the polymerization initiation due to the high volume of MBA molecules.

The plateau values reached by G' for poly(N-t-BAA) in water/ethanol mixture are of the same order of magnitude for samples obtained by radical polymerization in absence or presence of MBA (i.e., 13.700×10^3 Pa and 15.996×10^3 Pa for samples 1 and 6 from Table 1). The polymer obtained in the absence of any crosslinker (sample 1) and the chemical network of poly(N-t-BAA) (sample 6) give G' and G'' values higher than those corresponding to crosslinking with LRD. The viscoelastic moduli of poly(N-t-BAA) obtained in presence of LRD in water/ethanol mixture are lower due to the weaker physical interactions established between LRD platelets and polymer chains.

The loss tangent ($\tan \delta$), which is the ratio between G'' and G' , gives an indication concerning the degree of viscoelasticity of the sample. The lower value of $\tan \delta$ for samples obtained in the presence of high content of LRD or MBA indicates more elastic entangled polymer networks.

The induction period values determined by rheology and turbidimetry were different because the first method presents a dynamic character and the turbidimetry is a static method. Fig. 2a shows the variation of turbidity during the radical polymerization of N-t-BAA in presence of different amounts of LRD. The addition of clay up to LRD/N-t-BAA = 0.20 does not change significantly the induction period (about 10 min). The further addition of clay determines the

increase of the induction period followed by its decrease (Fig. 2b). The induction time for a LRD/N-t-BAA ratio of 0.30 was about 20 min. For the highest content of LRD (LRD/N-t-BAA = 0.4), during the first 12 min a decrease of the turbidity was evidenced after that it increases (Fig. 2a).

According to phase diagram of LRD in water,²⁴ at low ionic strength, the LRD dispersion is in the liquid isotropic state up to 2% LRD, isotropic gel state between 2% and 3.5% clay and nematic gel state at concentration above 3.5% LRD. In Fig. 2b, the concentrations which separate the three domains corresponding to phase diagram of LRD aqueous dispersion are shown. It can be observed that the increase of the induction period corresponds to the clay concentration for which LRD dispersion is in a liquid isotropic state.

By turbidimetry (a static method) it was evidenced the separation process of non- and crosslinked polymer from the reaction medium. During the polymerization of N-t-BAA, four stages were identified in the turbidity variation: induction stage, polymerization, final stage of the reaction (when the turbidity reaches a plateau) and, finally, separation of the polymer (when the turbidity strongly decreases). In Fig. 2c is exemplified the variation of the turbidity during the polymerization for LRD/N-t-BAA = 0.20.

N-t-BAA polymerization in presence of LRD was also followed by rheology. In Fig. 3 it is exemplified the variation of G' and G'' as a function of reaction time for the polymerization in absence of any crosslinker and for LRD/N-t-BAA = 0.30.

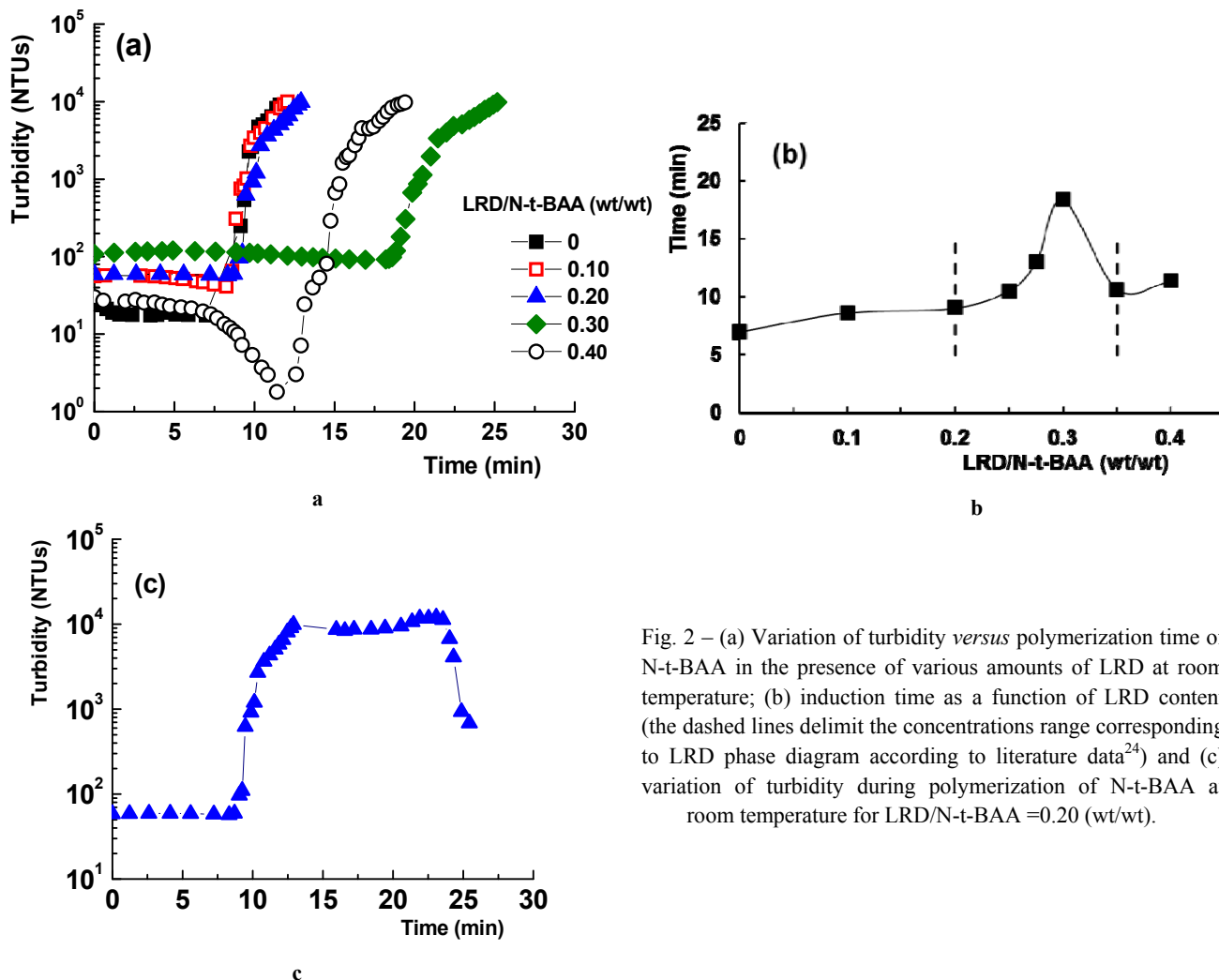
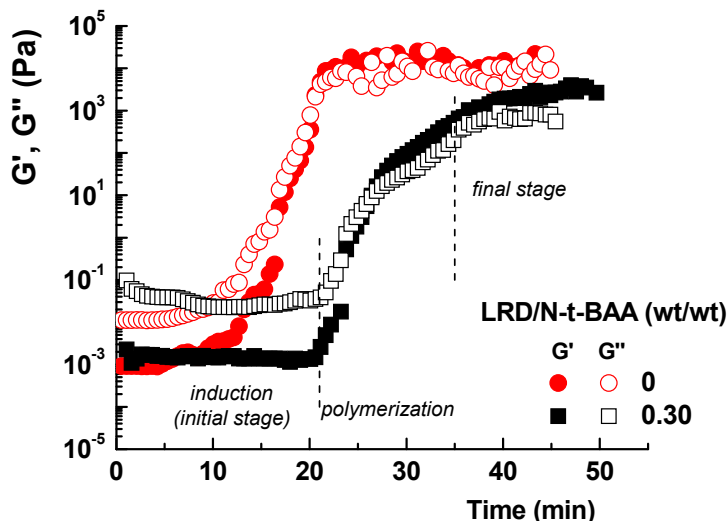


Fig. 2 – (a) Variation of turbidity *versus* polymerization time of N-t-BAA in the presence of various amounts of LRD at room temperature; (b) induction time as a function of LRD content (the dashed lines delimit the concentrations range corresponding to LRD phase diagram according to literature data²⁴) and (c) variation of turbidity during polymerization of N-t-BAA at room temperature for LRD/N-t-BAA = 0.20 (wt/wt).

Fig. 3 – Variation of viscoelastic moduli, G' and G'' during N-t-BAA polymerization in the absence/presence of LRD. The dashed lines delimit the three main stages during N-t-BAA polymerization in the presence of clay.



Initially, the values of the viscoelastic moduli are low and the systems show a like-liquid behaviour with $G'' > G'$. After a period of time, depending on the clay concentration, the viscoelastic moduli start to increase and G' value becomes equal or higher than the G'' one. The

polymerization process is considered to be complete when the viscoelastic moduli reach a plateau value. For the polymerization of acrylamide in the presence of APS, TEMED and LRD, the plateau values were reached after 1-2 hours.²³

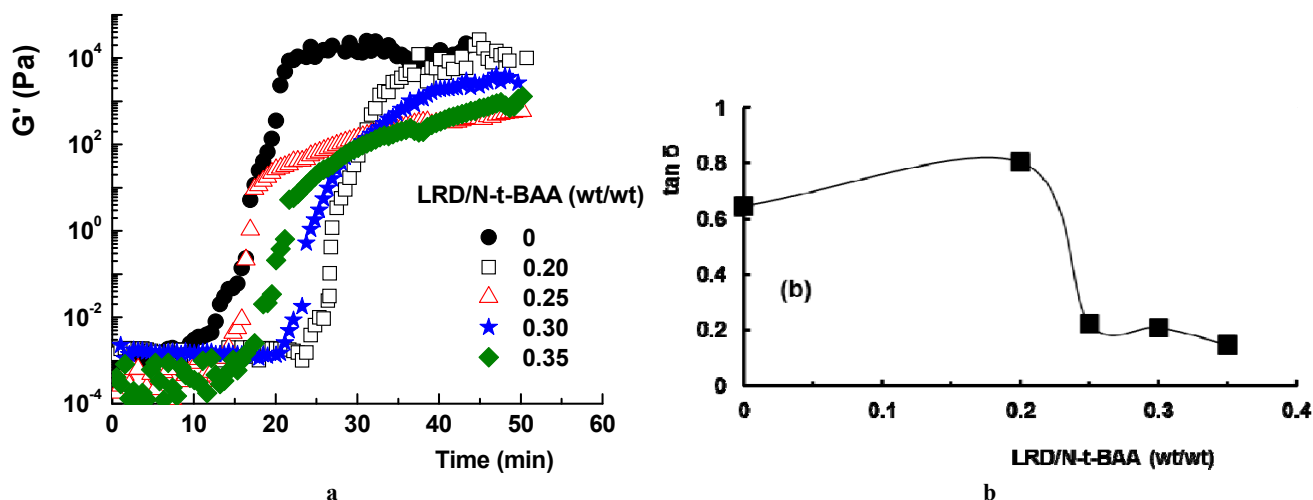


Fig. 4 – (a) Evolution of G' during the radical polymerization of N-t-BAA in absence and in presence of different amounts of LRD and (b) the variation of the loss tangent with LRD content.

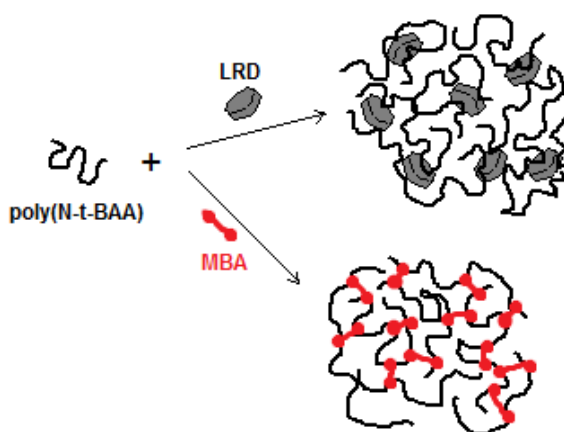


Fig. 5 – Schematic representation of poly(N-t-BAA) network in presence of LRD or MBA.

Recently, Strachota *et al.*¹⁵ proposed a mechanism of poly(*N*-isopropylacrylamide)-clay gel formation which involves three main stages: a) pregel stage, when the primary radicals are formed and the polymerization initiation occurs in the dispersion in which the clay platelets are well-dispersed and exfoliated (induction period); b) gelation, when a large fraction of polymer covers the clay disks and c) postgel stage, which involves the saturation of the clay surface with polymer and the bridges formation between platelets. Similarly, we identified by rheology the following stages for the N-t-BAA polymerization (Fig. 3): induction (small values of G' and G''), polymerization (pronounced increase G' and G'') and final stage of the reaction (the viscoelastic moduli reach a plateau). The fourth stage (polymer separation), evidenced by turbidimetry, was not revealed by rheological measurements due to their dynamic character.

Fig. 4a presents the variation of G' during the N-t-BAA polymerization.

One can be observed that, once the reaction is started, the viscoelastic moduli of samples in absence of LRD and with LRD/N-t-BAA = 0.20 reach very fast the final plateau (30 min and 1 h, respectively). In contrast to that, the samples containing a higher quantity of LRD (LRD/N-t-BAA > 0.20) show a continuous increase in viscoelastic moduli and the final plateau is attained after about 2 h. This delay observed in reaching the equilibrium values of rheological parameters can be caused by the physical aging process of LRD dispersions. It is well known that the LRD aqueous dispersions undergo an aging phenomenon which consists of a continuously change of their properties due to the aggregation of clay platelets and the equilibrium condition is reached after a period of time which depends on clay concentration and the addition of other components in system.²⁵

The plateau values of the viscoelastic moduli are given in Table 1. The addition of a small quantity of LRD does not change significantly the

values of G' , G'' and $\tan \delta$ (Table 1, Fig. 4b). All poly(N-t-BAA) samples have shown a solid-like behaviour ($\tan \delta < 1$). For a higher amount of LRD in system, $\tan \delta$ decreases due to the formation of stronger entangled network structures causing the increasing of G' .

The network structures of poly(N-t-BAA) obtained in the presence of LRD or MBA are schematic illustrated in Fig. 5.

EXPERIMENTAL

N-*t*-butylacrylamide (N-t-BAA), ammonium persulfate (APS) and *N,N,N',N'*-tetramethylethylenediamine (TEMED), *N,N'*-methylenebis(acrylamide) (MBA) were purchased from Aldrich and they were used without further purification. Laponite RD (LRD), which is a smectite clay with the chemical formula $\text{Na}^{+0.7}[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4]^{-0.7}$, was acquired from Rockwood Additives Limited U.K. Ethanol (from Aldrich) and millipore water (obtained using a Mili-Q PF apparatus) were used as solvents.

The solutions of 3 wt/vol % N-t-BAA were prepared in ethanol/water mixture (50/50, vol/vol). Stock solutions of APS and TEMED were prepared by dissolving 0.32 g of APS and 1 ml TEMED each in 40 ml distilled water. LRD dispersions with concentrations up to 4 wt% were prepared in deionized water under vigorous stirring for a few minutes. The clay dispersions were then ultrasonicated for 15 minutes and used as physical crosslinker within 2 hours from ultrasonication to prevent aging.

N-t-BAA polymerization, investigated in presence/absence of LRD and MBA, was initiated by APS/TEMED redox system. The monomer (or monomer/MBA mixture) solution (20 ml) and various amounts of LRD dispersion (with different concentrations) were mixed. Then, 4 ml of each stock solution of TEMED and APS were added into monomer (with/without physical and chemical crosslinkers) solution and it was stirred for 60 s before being introduced in the rheometer or turbidimeter.

The rheological measurements were carried out at 20 °C using a Bohlin CVO Rheometer with parallel plate geometry (60 mm diameter) and thermal control by Peltier effect. The evolution of the viscous (or loss) modulus (G'') and the elastic (or storage) modulus (G') during N-t-BAA polymerization was followed at a shear stress of 1 Pa and a frequency of 1 rad/s. The turbidity of polymerization systems was monitored at room temperature by using an HACH 2100AN turbidimeter. The moment when the sample was loaded into the measuring device was considered as the starting time ($t = 0$).

CONCLUSIONS

Effect of the crosslinker concentration and type on N-t-BAA polymerization in the presence of APS and TEMED as initiator and catalyst, respectively, has been investigated by rheology and turbidimetry. The rheological measurements revealed that the polymerization in the presence of MBA (chemical crosslinker) had the highest induction period (about 80 min) which decreased significantly by using LRD as physical crosslinker (about 25 min). For clay/monomer ratios between

0.20 and 0.35, an increase of polymerization induction time has been evidenced. The plateau viscoelastic parameters of poly(N-t-BAA) obtained by radical polymerization indicated that the network structure formation is delayed in the presence of physical or chemical crosslinkers.

The turbidity evolution during the polymerization process revealed four stages during the N-t-BAA polymerization: reaction induction, polymerization, final stage of the reaction and polymer separation.

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